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# Deca-Arylsamarocene: An Unusually Inert Sm(II) Sandwich Complex

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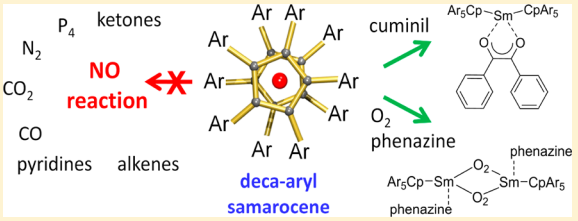
Supporting Information

**ABSTRACT:** Samarocene sandwich complexes with superbulky penta-arylcyclopentadienyl ligands have been prepared and were structurally characterized: $[(4\text{-EtC}_6\text{H}_4)_5\text{C}_5]_2\text{Sm}$ (**1**) and $[(4\text{-}i\text{PrC}_6\text{H}_4)_5\text{C}_5]_2\text{Sm}$ (**2**). Analogous to the previously reported synthesis of $[(4\text{-}n\text{BuC}_6\text{H}_4)_5\text{C}_5]_2\text{Sm}$, reaction of $(\text{DMAT})_2\text{Sm}\cdot(\text{THF})_2$ (DMAT = 2-$\text{Me}_2$N-$\alpha$-$\text{Me}_3$Si-benzyl) and the appropriate $\text{Ar}_5\text{C}_5\text{H}$ ligand gave **1** (66% yield) and **2** (59% yield). In contrast to the high reactivity of $\text{Cp*}_2\text{Sm}$, complex **1** has been shown to be surprisingly stable toward reaction with a large variety of reagents. Even under forcing conditions, no reaction with $N_2$, CO, $CO_2$, pyrazine, *trans*-stilbene, pyridine, $P_4$, and benzophenone was observed. Complex **1** reacts with cuminil ArC(O)C(O)Ar (Ar = 4-$i$PrC$_6$H$_4$) to yield the Sm(III) sandwich complex $[(4\text{-EtC}_6\text{H}_4)_5\text{C}_5]_2\text{Sm}[\text{ArC(O)C(O)Ar}]$ (**3**), which could be isolated in 83% yield as a dark-red crystalline material. Complex **2** reacts with oxygen in the presence of phenazine to yield the bimetallic Sm(III) complex $[(4\text{-}i\text{PrC}_6\text{H}_4)_5\text{C}_5\text{Sm}(\eta^1\text{-phenazine})]_2(\mu{:}\eta^2\text{-}\eta^2\text{-O}_2)_2$ (**4**) in 25% yield as dark-red crystals. The unusually high redox-stability of deca-arylsamarocenes originates from steric hindrance of the Sm metal center.




## INTRODUCTION

Since its discovery by Evans et al. in the 1980s, the samarocenes $\text{Cp*}_2\text{Sm}$ and $\text{Cp*}_2\text{Sm}\cdot(\text{THF})_2$ have been subject to a large number of reactivity studies (Scheme 1).[1−6] The typically bent sandwich-type complex $\text{Cp*}_2\text{Sm}$ has remarkably strong reducing properties allowing even for reduction of the generally inert $N_2$ to form $(\text{Cp*}_2\text{Sm}^{\text{III}})(\text{N}_2^{2-})$.[5]

Introduction of larger Cp ring substituents like $i$Pr[7] straighten the sandwich molecule, but not much is known on the reactivity of these species. The samarocene with bulky 1,2,4-$t\text{Bu}_3\text{C}_5$ ligands was found to be slightly bent (167°), but in contrast to $\text{Cp*}_2\text{Sm}$ showed no reductive cleavage of alkyl isocyanides, and instead a simple monoadduct was isolated.[8] Very recently, Trifonov and co-workers introduced the decabenzylsamarocene complex $(\text{Bn}_5\text{C}_5)_2\text{Sm}$,[9] a complex that in the solid state is bent (141.8°) and in which two aromatic rings strongly coordinate to Sm. The latter Ph···Sm coordination is favored over metal interaction with polar ligands like THF, DME, TMEDA, or $\text{PMe}_3$. The complex was in contrast to $\text{Cp*}_2\text{Sm}$ hardly reactive toward small molecules like $H_2$, $SiH_4$, $N_2$, or CO or to various unsaturated compounds containing C═C or C≡C bonds. It has been suggested that this inert behavior originates from the rather strong Ph···Sm interactions.

In 2008, we[10] and others[11] introduced metallocene complexes of the lanthanides containing $\text{Ar}_5\text{C}_5$ ligands. Although the ligand $\text{Ph}_5\text{C}_5\text{H}$ is readily accessible, the extremely poor solubility of its metallocenes limited synthetic access to these species: the metallocenes of Yb and Sm complexes (the complexes are insoluble in aromatic solvents and dissociate in polar solvents).[12] Whereas Deacon and co-workers circumvented this problem by using a redox-transmetalation/protolysis (RTP) protocol, we solubilized the complexes by introduction of an alkyl tail in the *para*-position of each phenyl ring, a ligand we abbreviated as $\text{Cp}^{\text{BIG}}$ (4-$n$Bu-C$_6$H$_4$)$_5$C$_5$), but for consistency here describe as $\text{Cp}^{\text{Ar-Bu}}$. It is noteworthy that the deca-arylsamarocene complex $\text{Cp}^{\text{Ar-Bu}}{}_2\text{Sm}$ has first been prepared by reacting a $\text{Sm}^{\text{III}}$ precursor with $\text{Cp}^{\text{Ar-Bu}}\text{H}$ (Scheme 2), a spontaneous reduction that in light of the strongly negative reduction potential ($E_{1/2}$ $\text{Sm}^{\text{III}}/\text{Sm}^{\text{II}}$ = −1.55 V)[13] is highly remarkable. Extensive investigations of the physical properties of $\text{Cp}^{\text{Ar-Bu}}{}_2\text{Sm}$ indeed confirm the +II oxidation state of the metal.[14] It is possible that this unexpected $\text{Sm}^{\text{III}} \rightarrow \text{Sm}^{\text{II}}$ transition may be explained with sterically induced-reduction (SIR).[15] Careful analysis of the metallocene's crystal structure, however, also suggests a significant contribution of secondary $\text{Cp}^{\text{Ar-Bu}}\cdots\text{Cp}^{\text{Ar-Bu}}$ bonding interactions to its unusual stability. Paradoxically, the large $\text{Cp}^{\text{Ar-Bu}}$ ligands do not repel but attract each other. Each aryl ring in the $\text{Cp}^{\text{Ar-Bu}}$ ligands is engaged in a C−H···$\pi$ interaction with the aromatic system of an aryl ring on the neighboring $\text{Cp}^{\text{Ar-Bu}}$ ligand (Scheme 2).[16] Although such nonclassical C−H···C hydrogen bridges are weak (2−5 kcal/mol),[17] the presence of 10 of such interactions per metallocene can result in substantial stabilization.[18−20] Solutions of $\text{Cp}^{\text{Ar-Bu}}{}_2\text{Sm}$ in toluene are stable up to at least 130 °C, but its stability toward small and/or reactive molecules has hitherto not been studied. Herein we present comprehensive investigations toward the reactivity of deca-arylsamarocenes and compare our results with chemistry known for $\text{Cp*}_2\text{Sm}$.

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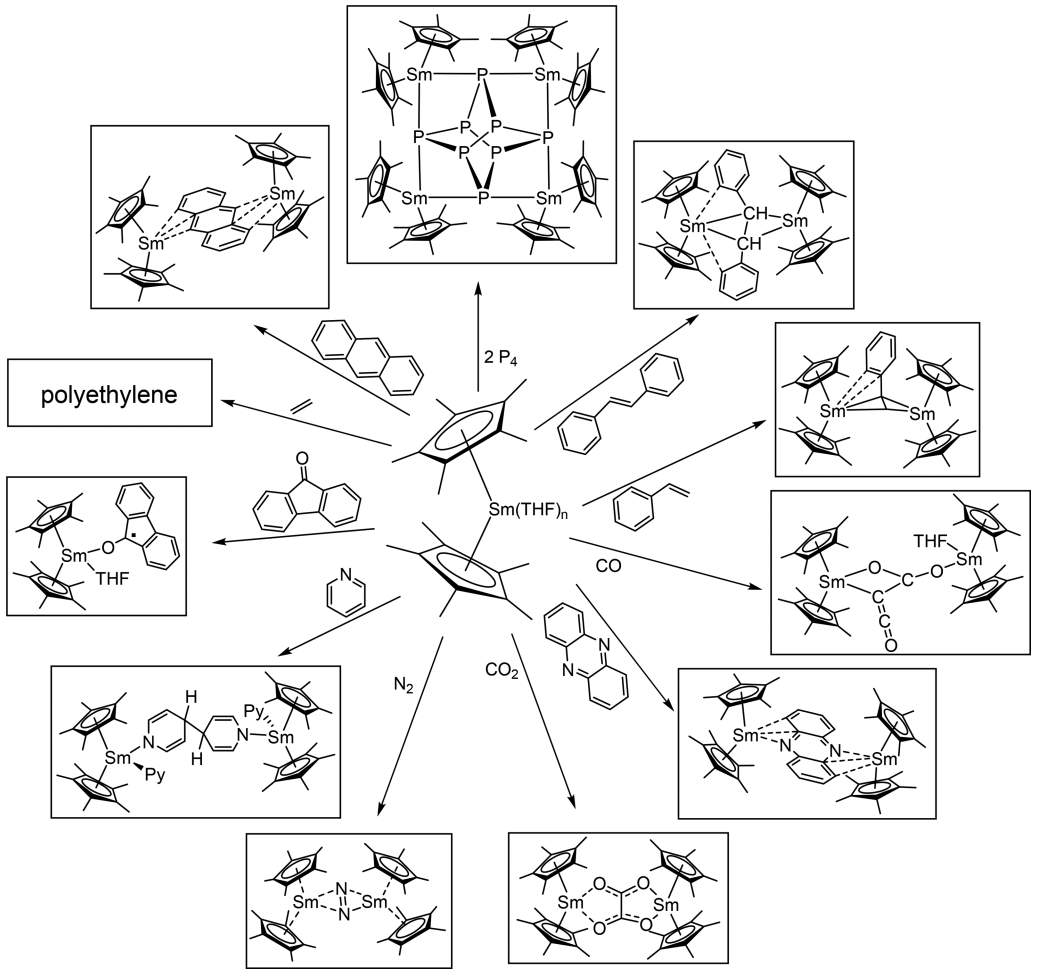
**Scheme 1. Versatile Reactivity of Deca-Methylsamarocene: $Cp^*_2Sm\cdot(THF)_n$ ($n$ = 0, 2)**




## RESULTS AND DISCUSSION

**Synthesis of Bulky Samarocene Complexes.** The introduction of *n*Bu substituents in the *para*-position of the Ph groups had a large impact on the solubility of the metallocenes. Whereas metallocenes containing the $Ph_5C_5$ ligand do not dissolve in apolar solvents, the samarocene $Cp^{Ar\text{-}Bu}{}_2Sm$ is extremely soluble, even in aliphatic solvents like hexane. During the course of our studies we found that this extremely high solubility is also a limitation that hinders, or in some cases even prohibits, product isolation by crystallization. For this reason we decreased the solubility of the metallocene complex by using modified ligands that contain shorter alkyl substituents: $(4\text{-Et-}C_6H_4)_5C_5H$, abbreviated as $Cp^{Ar\text{-}Et}$, and $(4\text{-}i\text{Pr-}C_6H_4)_5C_5H$, abbreviated as $Cp^{Ar\text{-}iPr}$. These ligands were prepared starting from $Cp_2ZrCl_2$ and 4-R-$C_6H_4Br$ (R = Et or *i*Pr) using a modified procedure published by Dyker et al.[21] in isolated yields of 74% ($Cp^{Ar\text{-}Et}H$) and 22% ($Cp^{Ar\text{-}iPr}H$). Similar to the preparation of $Cp^{Ar\text{-}Bu}{}_2Sm$, the two samarocene sandwich complexes $(Cp^{Ar\text{-}Et})_2Sm$ (**1**) and $(Cp^{Ar\text{-}iPr})_2Sm$ (**2**) were prepared by heating a solution of $(DMAT)_2Sm\cdot(THF)_2$ (DMAT = 2-$Me_2N$-$\alpha$-$Me_3Si$-benzyl) and 2.1 equiv of the appropriate cyclopentadienyl ligand in toluene at 100 °C for 18 h (Scheme 2, bottom). The products could be crystallized from a cold toluene/pentane mixture and were isolated as dark-red needles in 66% (**1**) and 59% (**2**) yield. Sandwich complexes **1** and **2** are thermally very stable. No decomposition of solutions of **1** and **2** in toluene-$d_8$ was observed after prolonged heating up to 130 °C. X-ray analyses on **1** (Figure 1) showed that this sandwich complex is, from a structural point of view, identical to $Cp^{Ar\text{-}Bu}{}_2Sm$. Complex **1** is centrosymmetric with an inversion center on Sm and two parallel $\eta^5$-Cp rings. The displacement factors for Sm indicated disorder of this atom in a plane parallel to the Cp rings. A similar situation was observed for Sm in $Cp^{Ar\text{-}Bu}{}_2Sm$.[10] Although Sm disorder in the latter structure was treated by refinement with large anisotropic thermal parameters, the structure of complex **1** was refined with a disorder model in which the electron density of the Sm atom is located at two positions slightly away from the inversion center. Like in $Cp^{Ar\text{-}Bu}{}_2Sm$, the samarocene **1** has parallel ligands ($Sm\text{–}Cp_{center}$: 2.504(5) and 2.521(5) Å) and a slightly bend $Cp_{center}\text{–}Sm\text{–}Cp_{center}$ arrangement (166.9(1)° and 168.0(1)°). Like in $Cp^{Ar\text{-}Bu}{}_2Sm$, the large $Cp^{Ar\text{-}Et}$ ligands attract each other which is apparent from short C–H···C($\pi$) interactions that range from 2.68 to 2.87 Å (average: 2.73 Å; cf. $Cp^{Ar\text{-}Bu}{}_2Sm$: 2.67 Å); for comparison, H atoms have been placed at idealized positions with C–H is 1.08 Å. The crystal quality of complex **2** was poor. As its structure is expected to be similar to that of **1**, we refrained from further structural characterization. Most reactivity studies have been performed with complex **1**. There is no noticeable difference in reactivity between **1** and **2** but in some cases it was easier to obtain crystalline products when using complex **2**.



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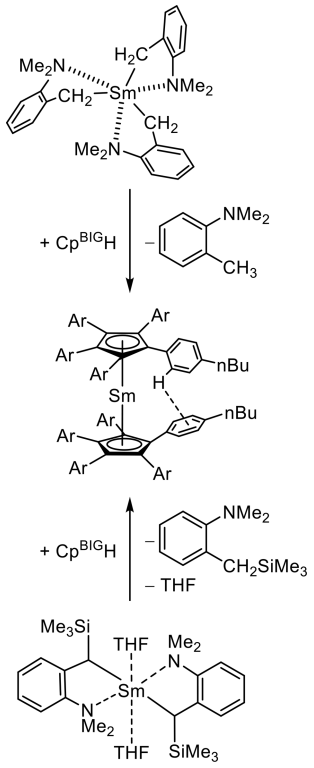
**Scheme 2. Synthesis of Deca-Arylsamarocenes Starting from $Sm^{III}$ (Top) or $Sm^{II}$ (Bottom) Precursors**



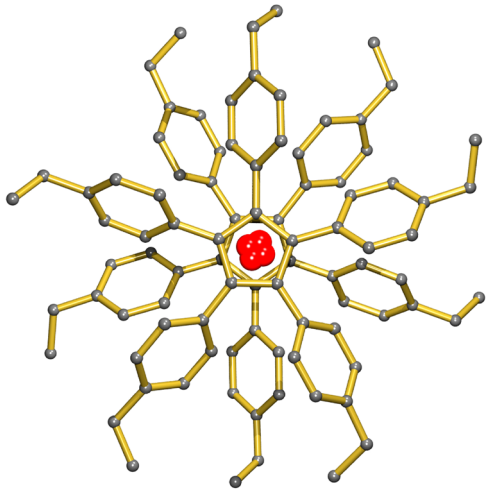



**Figure 1.** Crystal structure of the centrosymmetric samarocene complex $Cp^{Ar\text{-}Et}{}_2Sm$ (**1**). The Sm atom is disordered and was isotropically refined over two positions slightly away from the inversion center.

**Attempted Reactions of 1 with $N_2$, CO, $CO_2$, *trans*-Stilbene, Styrene, Ethylene and $P_4$.** Samarocene $Cp^*{}_2Sm$ slowly reacts already at room temperature with $N_2$ (Scheme 1).[5] As we found under similar conditions no evidence for a reaction of the herein synthesized samarocenes with $N_2$, a steel autoclave with complex **1** was pressurized with 50 bar of $N_2$. Solid state samples as well as solutions of **1** in benzene or toluene gave at this pressure and temperatures in the range of 20−50 °C no conversion and in all cases the unreacted samarocene **1** was isolated quantitatively. Since the reaction of $Cp^*{}_2Sm$ with $N_2$ is reversible,[5] we also studied a solution of **1** under $N_2$ pressure (4 bar) by NMR spectroscopy, both at room temperature and at 110 °C. In contrast to the smooth reaction of $Cp^*{}_2Sm$ with $N_2$, no reaction between **1** and $N_2$ was observed.

Evans et al. published that $Cp^*{}_2Sm\cdot(THF)_2$ reacts with CO, under formation of a ketene carboxylate Sm(III) bimetallic complex (Scheme 1).[22] In strong contrast, reaction of the bulky samarocene complex **1** with up to 4 bar of CO (99.997%) pressure at 110 °C for 24 h did not give any conversion and the starting material was quantitatively isolated. As traces of impurities may play a role in the reaction of $Cp^*{}_2Sm\cdot(THF)_2$ with CO,[23] it cannot be excluded that the inertness of **1** toward CO may be due to the absence of certain impurities.

$Cp^*{}_2Sm\cdot(THF)_2$ reacts with $CO_2$ in THF at room temperature under formation of the bimetallic Sm(III) oxalate complex $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2CCO_2)$; Scheme 1.[6] Although the isolated yield was high, the crystal structure is of poor quality. A related samarium oxalate with a higher quality X-ray structure was published in 2003.[24] Recent DFT calculations elucidated the reaction mechanism for this oxidative coupling of $CO_2$.[25] An example from 2006 shows a Sm(II) porphyrinogen complex which is oxidized to its carbonate-bridged bimetallic $Sm^{III}$ complex.[26] In strong contrast, no reaction was observed between a toluene solution of **1** and 4 bar of $CO_2$ at 110 °C for 24 h.

Samarocene complexes have been shown to catalytically isomerize *cis*-stilbene to *trans*-stilbene at a rate of 15 $h^{-1}$ ($Cp^*{}_2Sm\cdot(THF)_2$) and 840 $h^{-1}$ (solvent free $Cp^*{}_2Sm$).[1a] Reaction of solvent-free $Cp^*{}_2Sm$ with 0.5 equiv of either *cis*-stilbene or *trans*-stilbene gave the bimetallic complex $(Cp^*{}_2Sm)_2(PhCHCHPh)$; Scheme 1.[1a] In strong contrast, reaction of **1** and *trans*-stilbene at 110 °C for 24 h gave no conversion.

Styrene reacts instantaneously with $Cp^*{}_2Sm$ at room temperature to form the red-maroon Sm(III) complex $[(Cp^*{}_2Sm)_2(\mu\text{:}\eta^2\text{:}\eta^4\text{-}PhCHCH_2)]$; Scheme 1.[1a] Interestingly, addition of THF to this complex gave a spontaneous Sm(III) → Sm(II) reduction and free styrene and $Cp^*{}_2Sm\cdot(THF)_2$ could be isolated. A solution of **1** in $C_6D_6$ was heated in the presence of styrene to 80 °C. NMR spectra showed no change in the intensity of the signals of the complex but styrene olefinic signals disappeared quickly. This conversion of styrene is consistent with the well-known thermally induced styrene polymerization.[27] Complex **1**, however, remained unreacted and is inert toward styrene. $Cp^*{}_2Sm$ reacts with ethylene to polyethylene; Scheme 1.[2] In strong contrast, no reaction between **1** and 1 bar of ethylene at 110 °C for 24 h was observed.

The reduction of elemental P to various (multi)cyclic $P_x^{y-}$ ions has been extensively studied in the last decades and multiple reviews have been published.[28] Structures with various polyphosphide ions include $P_4^{2-}$, $P_5^-$ ions[29,30] and the $P_6^{4-}$ unit in $M_4P_6$ (M = K,[31] Rb,[32] Cs[33]). Prominent polyphosphide clusters contain $[P_7^{3-}]$[34] and $[P_{11}^{3-}]$ ions.[30] Reaction of $Cp^*{}_2Sm$ with $P_4$ vapor gave formation of a tetranuclear Sm(III) complex that contains a unique $P_8^{4-}$ anion; Scheme 1.[35] As dimerization of elemental $P_4$ to $P_8$ is enthalpically disfavored,[36] Roesky et al. suggested that the formation of the $P_8^{4-}$ ion is induced by electron transfer from Sm(II) to $P_4$.[35] In strong contrast, reaction of **1** and $P_4$ at 80 °C for 18 h gave no conversion.



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**Reaction of 1 with *aza*-Heterocycles.** Evans et al. also extensively studied the reactivity of $Cp^*_2Sm$ with polycyclic aromatic hydrocarbons and related *aza*-heterocycles.[37] They isolated a series of complexes with reduced aromatics that give insight into the reducing properties of $Cp^*_2Sm$. For example, anthracene and pyrene both reacted fast with $Cp^*_2Sm$ in a 1/2 ratio (aromatic substrate/complex) to form stable complexes in which a reduced aromatic substrate bridges two $Cp^*_2Sm(III)^+$ fragments (Scheme 1). As the second reduction potential of anthracene is $E_{1/2}$ = −2.44 V vs NHE,[38] this suggests that $Cp^*_2Sm$ may reduce aromatic substrates with a double reduction potential up to this value. In the case of phenazine, which has a first reduction potential of −0.120 V vs NHE,[39] and a second reduction potential of −0.364 V,[40] the reduced Sm(III) complex $(Cp^*_2Sm)_2(\mu{:}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)$ is formed in quantitative yield; Scheme 1.[37] A paper from 2008 reports on the reaction of $Cp^*_2Yb(II)$ with tetra-(2-pyridyl)-substituted phenazine that formed a product in which a doubly reduced phenazine ligand is bridged by two $Cp^*_2Yb(III)^+$ fragments.[41] Although Trifonov's $(Bn_5C_5)_2Sm^{II}$ hardly showed any reactivity with small molecules and unsaturated compounds, in reaction with phenazine the complex $[(Bn_5C_5)_2Sm^{III}]$(phenazine), containing a doubly reduced phenazine$^{2-}$ ion, was isolated.[9] In strong contrast, reaction of **1** and phenazine at 110 °C for 24 h did not lead to any reaction and the starting material was obtained quantitatively.

Evans et al. showed in 2012 that both $Cp^*_2Sm{\cdot}(THF)_2$ and $TMP_2Sm$ (TMP = $Me_5C_4P$) reacted fast with pyridine, but gave different products.[42] $TMP_2Sm$ formed the black Sm(II) pyridine adduct $TMP_2Sm{\cdot}(py)_2$ (py = pyridine).[42] Treatment of $Cp^*_2Sm{\cdot}(THF)_2$ in diethyl ether with a slight excess of pyridine gave a red bimetallic complex in which a C−C coupled bipyridinate ligand bridges two $Cp_2{}^*Sm(III)^+$ fragments; Scheme 1.[42] In strong contrast, no reaction between **1** and pyridine at 60 °C for 24 h was observed. It is of interest to note that addition of the polar solvent THF to $(Ph_5C_5)_2Yb$ leads to ligand dissociation and formation of the solvent-separated-ion-pair $[Yb^{2+}{\cdot}(THF)_6][Ph_5C_5^-]_2$.[11] The stability of $Cp^{Ar\text{-}Bu}{}_2Sm$ in the polar solvent pyridine is likely due to the larger size and lower Lewis acidity (softer nature) of $Sm^{2+}$ versus $Yb^{2+}$.

As pyrazine (1,4-diazabenzene) has a reduction potential of $E_{1/2}$ = −1.57 V vs a mercury electrode,[43] it is easier to reduce than pyridine ($E_{1/2}$ = −2.15 V vs a mercury electrode). Hitherto only a few $Ln^{III}$ complexes containing neutral pyrazine liagnds are known, e.g., $(Cp_3Yb)_2(\mu\text{-}NC_4H_4N)$.[44] We are not aware of examples of a lanthanide complex with a reduced pyrazine ligand. Despite the substantially lower reduction potential of pyrazine compared to pyridine, reaction of **1** with pyrazine at 80 °C for 18 h did not give any conversion.

**Reaction of 1 with Ketones.** Sandwich complexes with bulky scorpionate ligands ($Tp^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate) have been shown to stabilize complexes with radical anions and allow isolation of these reactive species. For example, addition of phenantrenequinone ($C_{14}H_8O_2$) to $Tp_2Sm(II)$ resulted in formation of dark-red $(Tp^{Me2})_2Sm(\eta^2\text{-}O_2C_{14}H_8)$.[45] The radical anion nature of the ketone ligands is demonstrated by the strongly shifted $^1H$ NMR signals of the ligands, and by the intense colors of the complexes.[45] Moreover, the carbon oxygen bond lengths in these complexes are significantly longer compared to the unbound neutral ligand.[45] Hou et al. reacted $Cp^*_2Sm(II)$ in THF with fluorenone (20 min, 20 °C) and isolated the ketyl complexes $Cp^*_2Sm(OC_{13}H_8)(THF)$ in 71% yield; Scheme 1.[46] The fact that this fluorenone reduction worked equally well with the much milder reducing agent $Cp^*_2Yb(II)$,[46] motivated us to investigate the reaction of **1** with a series of organic ketones. Remarkably, a solution of **1** in $C_6D_6$ and benzophenone did not react even at 100 °C. Reactions with the more easily reduced fluorenone and 1,4-benzoquinone did give conversion, but in both cases only extremely thin plate-like crystals unsuitable for X-ray diffraction could be obtained. Reaction of a solution of **1** in benzene at 20 °C with cuminil (ArC(O)C(O)Ar, Ar = 4-*i*Pr$C_6H_4$), a substituted benzil with the highly reactive conjugated O═C—C═O fragment, led to formation of dark-red crystals suitable for X-ray diffraction. The crystal structure shows formation of $Cp^{Ar\text{-}Et}{}_2Sm[ArC(O)\text{-}C(O)Ar]$ (**3**) and is described in detail below (Figure 2, Scheme 3). Although paramagnetic, the $^1H$ NMR spectrum of the raw product, the excellent crystalline yield of 83% and a correct elemental analysis of the product suggests formation of only a single species.

**Reaction of 1 or 2 with $O_2$.** Selectively reacting highly air-sensitive organometallic complexes with strongly oxidizing agents such as $O_2$ can be very challenging. Literature examples of well-defined products from reactions of Ln(II) complexes with $O_2$ are scarce. To the best of our knowledge, the reaction of $Cp^*_2Sm$ with $O_2$ has not been published ($Cp^*_2Sm{-}O{-}SmCp^*_2$ was obtained by reaction of $Cp^*_2Sm$ with epoxides or NO).[47] The hydro-*tris*(pyrazolyl)-borate and hydro-*tris*(3,5-dimethylpyrazolyl)-borate complexes $(Tp^{H2})_2Ln$ and $(Tp^{Me2})_2Ln$ (Ln = Sm, Yb) were allowed to react with $O_2$ in toluene at −78 °C to yield the mononuclear superoxide complexes $(Tp^{H2})_2Ln(\eta^2\text{-}O_2)$ and $(Tp^{Me2})_2Ln(\eta^2\text{-}O_2)$, respectively.[48,49] In these *superoxide* complexes, $O_2^{1-}$ is side-on coordinated to the Ln(III) center. Using pyridine-N-oxide as an oxidizing agent, however, gave a dimeric peroxo complex $[(Tp^{Me2})_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$, where $O_2^{2-}$ is bridging symmetrically between two Sm(III) centers.[49]

In an attempt to isolate a well-defined Sm(III)-oxo species, we added two equivalents of $O_2$ to a degassed benzene or toluene solution of **1** at room temperature. This led to an immediate color change from brown-red to blue. $^1H$ NMR monitoring suggested full conversion within minutes after $O_2$ addition. However, repeated attempts to isolate any reaction product from this reaction mixture were unsuccessful. In contrast, addition of 1.5 equiv of $O_2$ to a degassed benzene or toluene solution of **2** *in the presence of two equivalents of phenazine* gave an instant color change from intense red to deep blue. This color change suggests formation of the radical $(Cp^{Ar\text{-}iPr})^{\bullet}$.[50] After ca. 5 min, the reaction mixture was concentrated to dryness and the brick-red solid product was washed with hexane to give an intensely dark-blue hexane solution and a brick-red powder. Cooling the blue hexane solution to −30 °C gave intensely red crystals. Single crystal X-ray diffraction confirmed the formation of the radical $(Cp^{Ar\text{-}iPr})^{\bullet}$, but the structure is highly disordered and only allows for conclusions concerning atom connectivity (see Figure S11 for an EPR spectrum). NMR spectra of the remaining brick-red solid suggest formation of a single, major product which was isolated in ca. 70% yield. Pentane vapor diffusion into a toluene solution of these solids afforded dark-red prism-shaped crystals, which were isolated in 25% yield. X-ray crystallography and CHN analysis confirm the formation of


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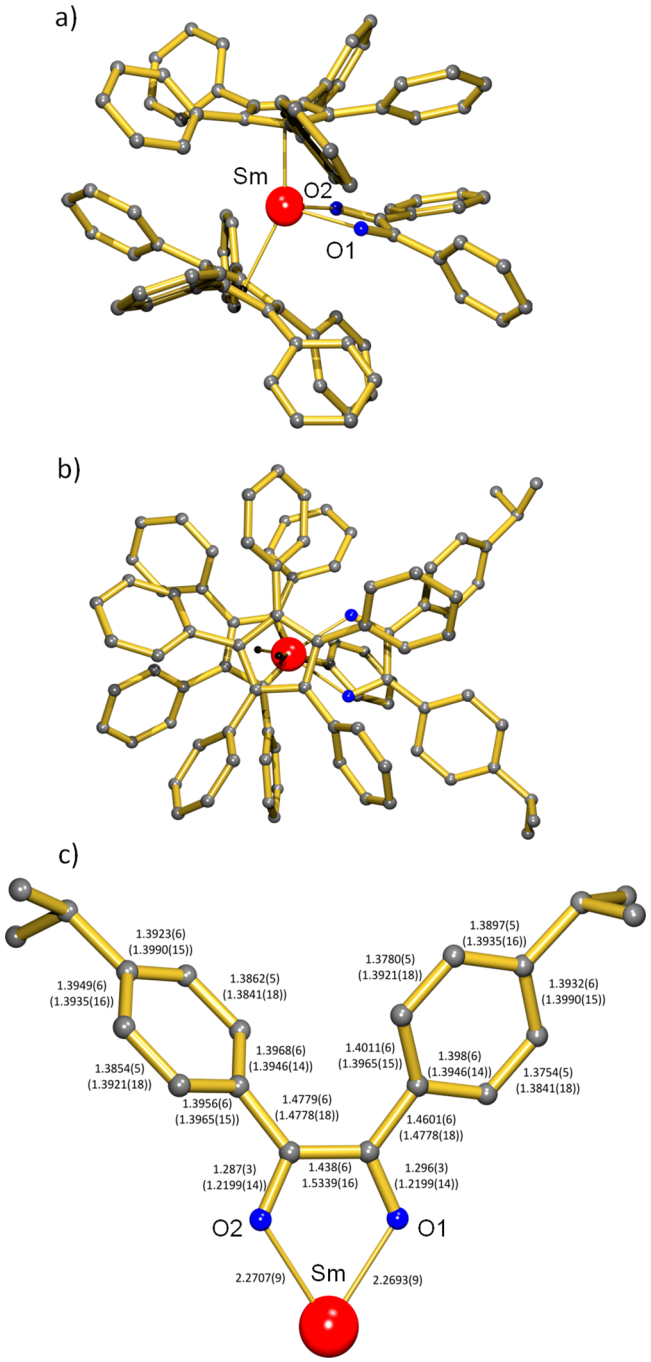


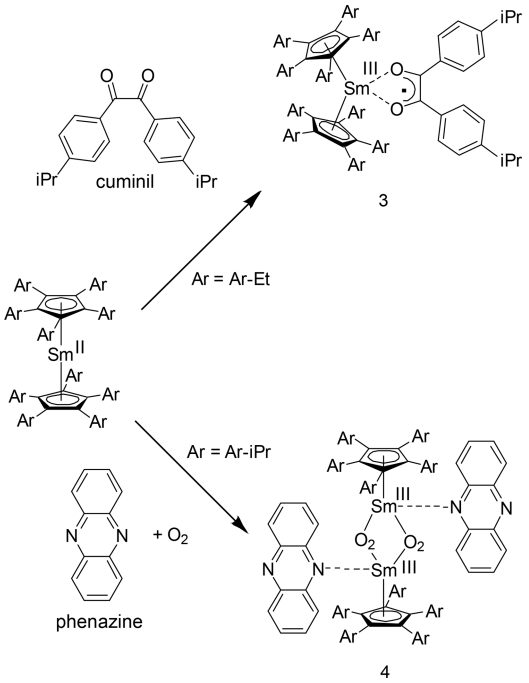

**Figure 2.** Crystal structure of $Cp^{Ar\text{-}Et}{}_2Sm[ArC(O)C(O)Ar]$ (**3**); H atoms, Et and *i*Pr substituents omitted for clarity. (a) Side-view and (b) top view. (c) Bond distances (Å) in the monoanionic, bidentate cuminil ligand compared with those in neutral cuminil (between parentheses).

the bimetallic Sm(III) complex $[Cp^{Ar\text{-}iPr}Sm(\mu{:}\eta^2\text{-}\eta^2\text{-}O_2)\text{-}(phenazine)]_2$ (**4**); Figure 3.

Although both $Cp^*{}_2Sm$ and $Cp^*{}_3Sm$ react with phenazine under formation of $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)$,[37,51] the bulky samorocenes **1** and **2** did not react with phenazine (vide supra). The phenazine, however, assists in the interception of a reaction intermediate in the oxidation of complex **2** by $O_2$. The crystal structure of **4** is discussed below.

**Crystal Structures of 3.** Complex **3** crystallized from cold pentane in 83% yield as dark-red blocks in the triclinic space

**Scheme 3. Reaction of Deca-Arylsamarocenes with Cuminil and Phenazine/$O_2$**[a]




[a]Product **3** contains a cuminil radical anion, and product **4** contains $O_2^{2-}$ ions and a neutral phenazine.

group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 2). The ArC(O)C(O)Ar ligand is slipped in between the two sterically demanding $Ar_5C_5$ ligands where it coordinates in an $\eta^2$-fashion to form a five-membered metallacycle that consists of two carbon atoms, two oxygen atoms and Sm(III). The only literature example of an $Ar_5C_5$ sandwich complex with an additionally coordinated ligand is $(Ph_5C_5)_2W = O$.[52] In this highly strained complex, the two $C_5$ rings coordinate in a slightly deviated $\eta^5$-fashion with W−C bond distances ranging from 2.322(6)−2.646(6) Å (average: 2.469 Å), and the $C_5$ rings are tilted in respect to each other by 24.5(4)° to allow for coordination of the oxygen atom. In addition, the three Ph substituents closest to the oxygen atom bent strongly out of the $C_5$ plane away from the metal center with $C_{ipso}-C_{C5}/C_5$ angles up to 13.6(5)°. A similar phenomenon is observed in the crystal structure of **3**. The aryl rings closest to the ArC(O)C(O)Ar ligand bent away from the Sm by 3.0(2)−11.2(2)°. Although the angle between the $Cp^{Ar\text{-}Et}$ planes in centrosymmetric complex **1** is exactly 0°, the two $Cp^{Ar\text{-}Et}$ rings in **3** form an angle of 31.4(1)° with respect to each other. This leads to slight ring slippage: the Sm−C distances in **3** vary from 2.743(2) Å to 2.866(3) Å (average: 2.803 Å) and the $Sm-ring_{centroid}$ distances measure 2.5245(10) and 2.5299(10) Å. These values are similar to those in **1** (Sm−C: 2.772 Å; $Sm-ring_{centroid}$ 2.527 Å).[10a] Given the smaller radius of Sm(III) compared to Sm(II), this might at first sight be unexpected. It is, however, in line with the higher coordination number of the Sm metal center in **3**.

The elongation of the C−O bond lengths in the cuminil ligand in **3** indicate single reduction of the ArC(O)C(O)Ar ligand to a radical anion and concomitant oxidation of Sm(II) to Sm(III). For a comparison of bond lengths, the crystal structure of neutral cuminil ligand has been determined (Figure 2c). The majority of the bond distances in neutral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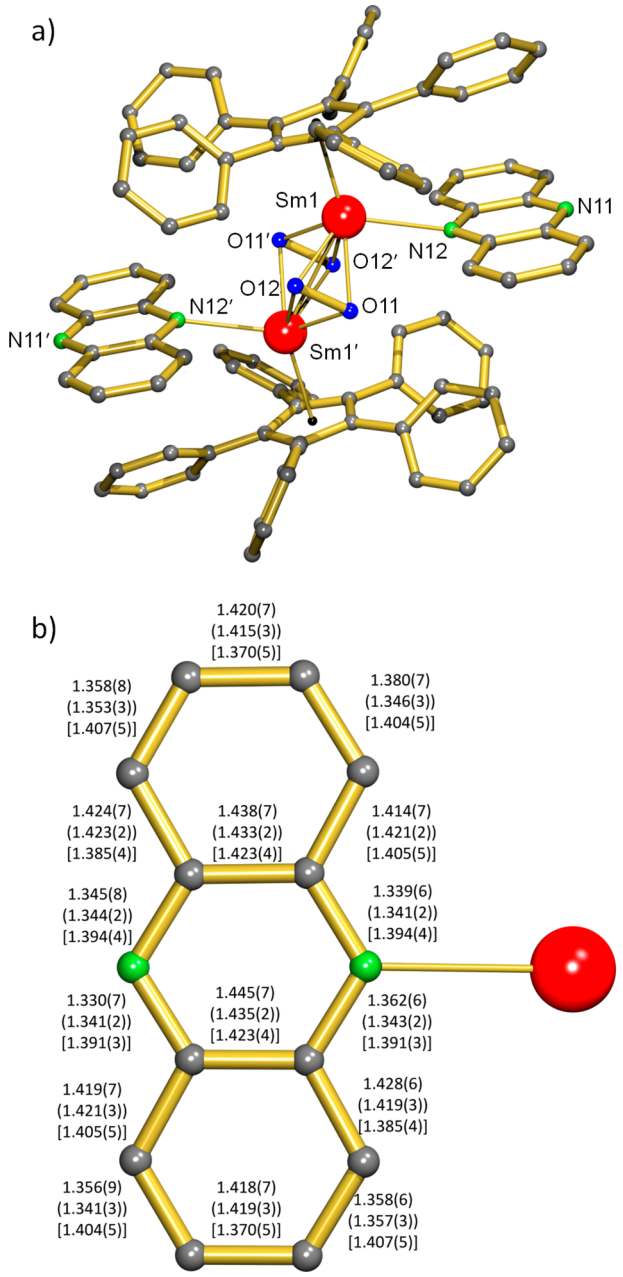


**Figure 3.** (a) Crystal structure of $[Cp^{Ar\text{-}iPr}Sm(\mu{:}\eta^2\text{-}\eta^2\text{-}O_2)(\text{phenazine})]_2$ (**4**); H atoms and *i*Pr substituents omitted for clarity. Selected bond distances (Å): Sm1−O11 2.338(3), Sm1−O12 2.273(3), Sm1−O11′ 2.268(3), Sm1−O12′ 2.347(3), Sm1−N12 2.685(4), O11−O12 1.517(4). (b) Bond distances (Å) in the monodentate phenazine ligand compared to those in in neutral phenazine (between parentheses)[58] and those in the dianionic phenazine ligand in $[Cp^*_2Sm(III)^+]_2[\text{phenazine}^{2-}]$ [between squared brackets][2] are given.

cuminil are within $2\sigma$ similar to those in the anionic cuminil ligand in **3**. However, the (O)C−C(O) bond distance in **3** has been shortened by approximately 0.0959 Å compared to neutral cuminil. Also the C−O bond distances in **3** are longer by approximately 0.0716 Å compared to those in neutral cuminil. This is indicative of a cuminil radical anion with a delocalized negative charge over the O−C−C−O unit. The C−O bond distances in fluorenone[53] and benzophenone[54] radical anions in Sm(III) complexes are 1.313(7) Å and 1.346(7) Å, respectively. Both are slightly longer than the C−O distance of 1.292(3) Å in **3**.

**Crystal Structure of 4.** Complex **4** crystallized as dark-red needles in the triclinic space group $P\bar{1}$ with two independent, but essentially similar, molecules in the asymmetric unit (Figure 3). In both independent bimetallic complexes there is a center of inversion located between the two samarium atoms. The Sm−$\text{ring}_{\text{centroid}}$ distances of 2.5142(19) and 2.5094(19) Å in complex **4** are essentially similar to that in **1**: 2.5016(3) Å. Although one expects shorter bond distances for Sm(III) than for Sm(II), the nearly equal Sm−$\text{ring}_{\text{centroid}}$ distances may be explained by a different coordination number for Sm in **4**. The O−O bond distances in **4** are 1.517(4) and 1.509(4) Å and are in the range expected for a peroxo $O_2^{2-}$ ligand.[55−57] Literature examples of complexes that contain a similar $(O_2)_2$ core include $[\{(CO_3^{2-})_4Ce(IV)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)_2]_4^-[C(NH_2)_3]_4^+ \cdot H_2O$ (O−O = 1.455(12) Å),[55] $K_2Na_2[\{(edta)Ce(IV)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)_2]\cdot 13H_2O$[56] (edta = ethylenediaminetetraacetic acid, O−O = 1.488(5) Å) and $Ln_4(O_2)_2Cl_8(py)_{10}$[57] (Ln = Sm: O−O = 1.538(3) Å, Ln = Eu: O−O = 1.522(4) Å), Gd (O−O = 1.538(5) Å); py = pyridine). In contrast, the O−O bond distance for the superoxide $O_2^{1-}$ anion in $Tp^{Me2}{}_2Sm(\eta^2\text{-}O_2)$ is much shorter: 1.319(5) Å.[48] The Sm−O distances in **4** are 2.338(3) and 2.273(3) Å. These distances are shorter compared to those observed in $Sm_4(O_2)_2Cl_8(py)_{10}\cdot Py$ (average 2.388 Å).[57]

Another intriguing feature of **4** is the presence of two neutral $\eta^1$-coordinating phenazine ligands. The neutrality of the phenazine ligand in **4** is evident from a comparison of its C−C and C−N bond distances with those in neutral phenazine[58] and those in $[Cp^*_2Sm(III)^+]_2[\text{phenazine}^{2-}]$;[3] see Figure 3. Complex **4** is an unique example of a lanthanide complex that bears a neutral $\eta^1$-coordinating phenazine ligand.

## CONCLUSIONS

The reactivity of the deca-arylsamarocene **1** with a large array of substrates has been evaluated and is compared to that of $Cp^*_2Sm$. Whereas the latter deca-methylsamarocene reacts with a wide variety of substrates, including inert gases like $N_2$, deca-arylsamarocenes are surprisingly stable. No reactions could be observed with $N_2$, CO, $CO_2$, *trans*-stilbene, styrene, ethylene, and $P_4$. Complex **1** also did not react with the N-containing heterocycles pyridine, pyrazine and phenazine. Likewise, the samarocene **1** does not react with ketones like benzophenone. Although reaction of the samarocenes **1** or **2** with the more reactive ketones, fluorenone and 1,4-benzoquinone did give conversion, products could not be characterized unambiguously. The diketone cuminil, ArC(O)-C(O)Ar, however, reacted smoothly with **1** under ambient conditions, and the product $Cp^{Ar\text{-}Et}{}_2Sm[ArC(O)C(O)Ar]$ (**3**) could be structurally characterized. X-ray diffraction studies indicate a radical anion formulation for the cuminil fragment. The deca-arylsamarocenes **1** and **2** both react with $O_2$, but only in the reaction of complex **2** could we trap the oxidation product by addition of phenazine and isolated dark-red needle-like crystals of constitution $[Cp^{Ar\text{-}iPr}Sm(O_2)(\text{phenazine})]_2$ (**4**). The O−O bond distance of 1.513(4) Å is typical for a peroxo $O_2^{2-}$ ligand, and the geometry of phenazine indicates neutrality.

This comprehensive reactivity study on deca-arylsamarocenes demonstrates an extraordinary paucity of redox reactivity. Their inert behavior toward a large series of reactants strongly contrasts with the high reactivity of


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$Cp^*_2Sm$. Although this may be explained by obvious differences in steric hindrance between $Cp^*_2Sm$ and deca-arylsamarocenes, there may be an electronic component as well. The Me substituents in Cp* are electron releasing and stabilize metals with a higher oxidation state, whereas aryl substituents in $Cp^{Ar\text{-}Et}$ can stabilize the negative charge on the cyclopentadienyl ligand by the mesomeric effect. The latter makes penta-arylcyclopentadienyl ligands poor electron donors and disfavor oxidation. There certainly is also an obvious steric argument. Whereas $Cp^*_2Sm$ has a bent structure, rendering the metal center easily accessible, the metal center in linear deca-arylsamarocenes is highly shielded by the ten phenyl groups that due to attractive interactions with each other are even bend toward the metal center. This increases steric shielding and effectively prevents metal-substrate interactions. The high stability of deca-arylmetallocenes may be exploited in applications where high metallocene stability and low chemical reactivity is desired.

## EXPERIMENTAL SECTION

**General Considerations.** All experiments were carried out in dry glassware under Ar using standard Schlenk-techniques (or in the inert Ar atmosphere of a glovebox) and freshly dried and degassed solvents (all solvents were dried over a column). Following reagents were obtained commercially: palladium(II) acetate (ABCR, 98%), tri-*tert*-butyl phospine (ABCR, 98%), *n*-butyllithium (2.5 M in hexanes), 1,2-diiodoethane (Sigma-Aldrich, 99%), samarium (Smart Elements, 99.99%), zirconocene dichloride (ABCR, 99%), oxygen (Linde, 5.0), carbon dioxide (Linde, 5.0), nitrogen (Linde, 5.0) and carbon monoxide (Praxair, 4.7) were used as received. $H_2$ (AGA, 99.9%) was passed over a column of $LiAlH_4$ prior to use. 1-Bromo-4-ethylbenzene (Apollo Scientific) and 1-bromo-4-isopropylbenzene (Matrix Scientific, 95%) were dried over $CaH_2$ and filtered prior to use. Phenazine (≥99%, Apollo Scientific) was dried as a solution in $CH_2Cl_2$ over $CaH_2$, filtered and concentrated to dryness prior to use. Cesium carbonate (Acros, 99.9%) was dried under high vacuum at 150 °C for 8 h prior to use. White phosphorus was freshly sublimed prior to use and stored in a glovebox under argon atmosphere. $(DMAT)_2Sm(THF)_2$[59] and 1,2-bis(4-isopropylphenyl)ethane-1,2-dione (cuminil)[60] were synthesized according to previously published procedures. NMR spectra were recorded on Varian Mercury 400, Varian Inova 500 or Bruker Advance 400 spectrometers. Elemental analysis was performed with an Hekatech Eurovector EA3000 analyzer or at the microanalysis lab Kolbe (Mülheim an der Ruhr, Germany). Crystal structures have been measured on a Bruker D8 Venture diffractometer with a Mo sealed tube X-ray source and a Photon100 CCD detector or an Agilent Supernova with a Mo microfocus source and Atlas S2 detector. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1838409 (**1**), 1838410 (**3**), 1838411 (**4**), 1838412 (cuminil). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223−336−033; E-mail: deposit@ccdc.cam.ac.uk).

**Synthesis of $(4\text{-}EtC_6H_4)_5C_5H$; $Cp^{Ar\text{-}Et}H$.** $Cs_2CO_3$ (91 g; 0.28 mol), DMF (ca. 400 mL), 1-bromo-4-ethylbenzene (54.1 g; 0.292 mol) and $Cp_2ZrCl_2$ (6.74 g; 0.0231 mol) were added to a large Schlenk flask. The solvent was degassed and $tBu_3P$ (4.2 g; 21 mmol) dissolved in DMF (3 mL) and solid $Pd(OAc)_2$ (1.30 g; 5.79 mmol) were added to the reaction mixture. The Schlenk flask was immersed in a preheated (130 °C) oil bath and kept at this temperature for 2 days. After cooling to ambient temperatures, $Et_2O$ (200 mL) and *para*-toluenesulfonic acid monohydrate (102 g; 0.586 mol) were added and the reaction mixture was stirred for 30 min and subsequently filtered over silica. The product was further extracted from deposits on the filter by extractions with several portions of $Et_2O$ (total: 800 mL) until the extracts were nearly colorless. The filtrate and washings were combined and concentrated to dryness under reduced pressure by stripping with several portions of toluene (ca. 100 mL) in order to remove most of the DMF. Subsequently, $Et_2O$ (ca. 500 mL) was added and the solution was washed carefully with a saturated $NaHCO_3$ solution (ca. 150 mL) three times. The organic layer was washed with brine (ca. 2 × 100 mL), dried on $Na_2SO_4$ and concentrated to dryness to isolate the crude product as a black tar. This black tar was further purified by filtration over silica in a Soxhlet apparatus using a pentane/diethyl ether (96/4) mixture. All volatiles from the filtrate were removed in vacuo to yield a yellowish sticky solid. The solid was washed with pentane several times to yield the product as an off-white powder (20.1 g; 34.3 mmol; 74%). $^1$H NMR (DCM-$d_2$, 499.86 MHz, 25 °C) $\delta$ 7.27 (d, $J$ = 8.1 Hz, 2H, ArCH), 7.15−7.11 (m, 10H, ArC*H*), 7.10 (d, $J$ = 8.1 Hz, 4H, ArCH), 7.00 (d, $J$ = 8.1 Hz, 4H, ArCH), 5.26 (s, 1H, CpH), 2.69 (q, $J$ = 7.6 Hz, 4H, Et−C$H_2$), 2.64 (q, $J$ = 7.6 Hz, 2H, Et−C$H_2$), 2.60 (q, $J$ = 7.6 Hz, 4H, Et−C$H_2$), 1.29 (t, $J$ = 7.6 Hz, 6H, Et−C$H_3$), 1.26 (t, $J$ = 7.6-Hz, 3H, Et−C$H_3$), 1.23 (t, $J$ = 7.6 Hz, 6H, Et−C$H_3$) ppm. $^{13}$C NMR (DCM-$d_2$, 125.70 MHz, 25 °C) $\delta$ 146.7 (2C, $sp^2$ CpCAr), 144.5 (2C, $sp^2$ CpCAr), 143.1 (2C, Ar-CEt), 142.69 (1C, Ar-CEt), 142.66 (2C, Ar-CEt), 136.5 (1C, Ar *ipso*-C), 134.5 (2C, Ar *ipso*-C), 133.8 (2C, Ar *ipso*-C), 130.5 (4C, ArCH), 129.3 (4C, ArCH), 128.8 (2C, ArCH), 128.4 (2C, ArCH), 127.8 (4C, ArCH), 127.7 (4C, ArCH), 61.7 (1C, CpCH), 28.9 (2C, Et-$CH_2$), 28.79 (2C, Et-$CH_2$), 28.77 (1C, Et-$CH_2$), 15.5 (2C, Et-$CH_3$), 15.39 (2C, Et-$CH_3$), 15.38 (1C, Et-$CH_3$) ppm. HRMS (ESI) calcd for $[M + H]^+$ 587.36723, found 587.36604. mp 133−134 °C. Anal. Calcd for $C_{45}H_{46}$: C, 92.10; H, 7.90%. Found: C, 91.98; H, 7.52%.

**Synthesis of $(4\text{-}iPrC_6H_4)_5C_5H$; $Cp^{Ar\text{-}iPr}H$.** $Cs_2CO_3$ (51 g; 0.16 mol), DMF (ca. 250 mL), 1-bromo-4-isopropylbenzene (29.9 g; 0.150 mol) and $Cp_2ZrCl_2$ (3.67 g; 0.0126 mol) were added to a large Schlenk flask. The solvent was degassed and $t\text{-}Bu_3P$ (2.30 g; 11 mmol) dissolved in DMF (3 mL) and solid $Pd(OAc)_2$ (700 mg; 3.12 mmol) were added. The Schlenk was immersed in a preheated (130 °C) oil bath and kept at that temperature for 2 days. After cooling to ambient temperature, $Et_2O$ (ca. 200 mL) and *para*-toluenesulfonic acid monohydrate (55 g; 0.32 mol) were added. After stirring for 30 min, the reaction mixture was filtered over silica with additional portions of $Et_2O$ (50 mL) until the washings were nearly colorless. The filtrate and washings were combined and concentrated to dryness under reduced pressure by stripping with several portions of toluene (ca. 100 mL). Subsequently, $Et_2O$ (ca. 500 mL) was added and the solution was washed carefully with a saturated $NaHCO_3$ solution (100 mL) three times. The organic layer was dried with brine (2 × 100 mL), dried on $Na_2SO_4$ and concentrated to dryness to isolate the crude product as a black tar. This black tar was further purified by filtration over silica in a Soxhlet apparatus using a pentane/diethyl ether (98/2) mixture. All volatiles from the filtrate were removed in vacuo to yield a yellowish sticky solid. The solid was washed with pentane several times to yield the product as an off-white powder (3.61 g; 5.49 mmol; 22%). $^1$H NMR (DCM-$d_2$, 499.86 MHz, 25 °C) $\delta$ 7.23 (d, $J$ = 8.0 Hz, 2H, ArCH), 7.15−6.90 (m, 18H, ArC*H*), 5.20 (s, 1H, Cp*H*), 2.88 (sept, $J$ = 7.0 Hz, 2H, *i*-Pr C*H*), 2.85 (q, $J$ = 7.6 Hz, 1H, *i*-Pr C*H*), 2.80 (sept, $J$ = 7.6 Hz, 2H, *i*-Pr C*H*), 1.23 (d, $J$ = 6.9 Hz, 12H, *i*-Pr C$Me_2$), 1.21 (d, $J$ = 6.9 Hz, 6H, *i*-Pr C$Me_2$), 1.18 (d, $J$ = 6.9 Hz, 12H, *i*-Pr C$Me_2$) ppm. $^{13}$C NMR (DCM-$d_2$, 125.70 MHz, 25 °C) $\delta$ 147.7 (2C, Ar *C*-*i*-Pr), 147.3 (2C, Ar *C*-*i*-Pr), 147.2 (2C, Ar *C*-*i*-Pr), 146.3 (2C, $sp^2$ CpC), 144.7 (2C, $sp^2$ CpC), 136.3 (1C, Ar *ipso*-C), 134.6 (2C, Ar *ipso*-C), 133.8 (2C, Ar *ipso*-C), 130.3 (2C, ArCH), 129.0 (2C, ArCH), 128.7 (1C, ArCH), 127.0 (1C, ArCH), 126.22 (2C, ArCH), 126.18 (2C, ArCH), 61.1 ($sp^3$ CpCH), 34.1 (1C, *i*-PrCH), 34.0 (2C, *i*-PrCH), 33.9 (2C, *i*-PrCH), 24.09 (2C, *i*-Pr$Me_2$), 24.05 (4C, *i*-Pr$Me_2$), 24.0 (2C, *i*-Pr$Me_2$), 23.9 (2C, *i*-Pr$Me_2$) ppm. HRMS (ESI) calcd for $[M + H]^+$ 657.44548, found 657.44418. mp 147−149 °C. Anal. Calcd for $C_{50}H_{56}$: C, 91.41; H, 8.59%. Found: C, 90.88; H, 8.22%. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.

**Synthesis of $[(4\text{-}EtC_6H_4)_5C_5]_2Sm$; $(Cp^{Ar\text{-}Et})_2Sm$ (1).** Solid $(4\text{-}EtC_6H_4)_5C_5H$ (3.04 g; 5.18 mmol) was added to a solution of $(DMAT)_2Sm\cdot(THF)_2$ (1.83 g; 2.59 mmol) in toluene (40 mL). The



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reaction mixture was stirred for 2 days at 90 °C and slowly cooled to ambient temperatures. Next, pentane (30 mL) was slowly condensed into the solution via vapor diffusion and after subsequent cooling to −30 °C overnight, the resulting dark-red crystalline material was filtered from the reaction mixture, washed with additional pentane and dried in vacuo to yield the desired product in good yield (2.25 g, 1.70 mmol, 66%). The $^1$H NMR spectrum shows at room temperature broad signals but at higher temperature sharpening of all signals is observed. $^1$H NMR (toluene-$d_8$, 499.86 MHz, 70 °C) $\delta$ = 13.50−12.30 (br s, 20H, ArC*H*), 10.30−10.00 (br s, 20H, ArC*H*), 4.70−4.50 (br s, 20H, Et−C$H_2$), 2.90−2.85 (br s, 30H, Et−C$H_3$) ppm. $^{13}$C NMR (benzene-$d_6$, 125.7 MHz, 25 °C) $\delta$ = 183.1 (quat, ArC), 170−162 (quat, ArC, br), 147.5 (ArCH), 136.7 (ArCH), 128.6 (CpC), 30.7 (Et$CH_2$), 19.8 (Et$CH_3$) ppm. Anal. Calcd for $C_{90}H_{90}Sm$: C, 81.76; H, 6.86%. Found: C, 81.75; H, 6.91%.

**Synthesis of [(4-*i*PrC$_6$H$_4$)$_5$Cp]$_2$Sm; (Cp$^{Ar\text{-}iPr}$)$_2$Sm (2).** Solid (4-*i*PrC$_6$H$_4$)$_5$CpH (2.55 g; 3.88 mmol) was added to a solution of (DMAT)$_2$Sm$^{II}$(THF)$_2$ (1.34 g; 1.89 mmol) in toluene (8 mL). The reaction mixture was stirred for 24 h at 75 °C and slowly cooled to ambient temperatures. Next, pentane (10 mL) was layered on top of the toluene solution. Diffusion of the hexane into the toluene gave dark-red crystals. The crystals were filtered, washed with pentane and dried in vacuo to obtain the desired product in good yield (1.62 g; 1.11 mmol; 59%). $^1$H NMR (benzene-$d_6$, 499.86 MHz, 80 °C) $\delta$ 13.15−11.65 (br s, 20H, ArC*H*), 10.32−9.88 (br s, 20H ArC*H*), 4.77−4.62 (br s, 10H, *i*−Pr−C*H*), 2.85−2.70 (br s, 60H, *i*-Pr-*Me*$_2$) ppm. $^{13}$C NMR (benzene-$d_6$, 125.70 MHz, 80 °C) $\delta$ 179.9 (ArC), 160.7 (ArC), 150.9 (ArCH), 133.4 (ArCH), 129.7 (CpC), 35.4 (*i*-Pr *C*H), 27.0 (*i*-Pr *Me*$_2$) ppm. Anal. Calcd for $C_{100}H_{110}Sm$: C, 82.14; H, 7.58%. Found: C, 81.86; H, 7.41%. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.

**Synthesis of Cp$^{Ar\text{-}Et}$$_2$Sm(cuminil) (3).** To a solution of **1** (190 mg; 0.144 mmol) in toluene (ca. 2 mL) was added cuminil (44.5 mg; 0.151 mmol). The reaction mixture was stirred at room temperature for 10 min and subsequently concentrated to dryness in vacuo. The obtained dark-red solids were recrystallized from cold pentane and the title compound could be obtained as dark-red crystals (192 mg; 0.119 mmol; 83%). $^1$H NMR (toluene-$d_8$, 399.83 MHz, 25 °C) $\delta$ = 50.65 (s), 42.29 (s), 6.80−6.65 (br s), 5.87 (s), 4.01 (s), 2.57 (t, $J$ = 7.5 Hz, 20H, Et$CH_2$), 0.88 (q, $J$ = 7.5 Hz, 30H, Et$CH_3$) ppm. $^{13}$C NMR (toluene-$d_8$, 125.70 MHz, 25 °C) $\delta$ = 165.2, 147.5, 143.3, 135.7, 129.2, 27.9, 16.7 ppm. Anal. Calcd for $C_{110}H_{112}O_2Sm$: C, 81.73; H, 6.98%. Found: C, 80.83; H, 6.81%. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date.

**Synthesis of [Cp$^{Ar\text{-}iPr}$Sm($\mu$:$\eta^2$-$\eta^2$-O$_2$)(phenazine)]$_2$ (4).** A solution of **2** (179 mg, 0.122 mmol) and phenazine (38 mg, 0.21 mmol) in toluene (ca. 1 mL) was exposed to a vacuum at room temperature for ca. 30 s at room temperature. Subsequently, 18 mL of 0.25 bar (0.19 mmol) $O_2$ was admitted using a calibrated gas bulb. The reaction mixture was stirred at room temperature for 5 min and all volatiles were removed in vacuo. The resulting dark blue sticky solid was washed with pentane (ca. 3 mL in portions) to remove the Cp$^{Ar\text{-}Et5\bullet}$ radical and a brick-red solid was obtained. Recrystallization from toluene/pentane at −20 °C afforded the title compound as dark-red crystals (31 mg; 0.015 mmol; 25%). $^1$H NMR (toluene-$d_8$, 499.86 MHz, −20 °C) $\delta$ = 8.71 (d, $J$ = 9.0 Hz, 2H, phenazine), 6.82 (pt, $J$ = 7.4 Hz, 2H, phenazine), 6.71 (br s, 10H, ArCH), 5.84 (d, $J$ = 7.4 Hz, 10H, ArCH), 3.86 (br s, 2H, phenazine), 2.15 (sept, $J$ = 6.8 Hz, 5H, C*H*Me$_2$), 0.72 (d, $J$ = 6.8 Hz, 30H, CH*Me*$_2$), −5.58 (br s, 2H, phenazine) ppm. $^{13}$C NMR (benzene-$d_6$, 125.70 MHz, 25 °C) $\delta$ = 150.84 (phenazine *C*N), 150.81 (phenazine *C*N), 144.9 (Ar *ipso*-C), 143.8 (ArC-*i*-Pr), 131.9 (phenazine *C*H), 131.7 (phenazine *C*H), 129.9 (phenazine *C*H), 129.1 (phenazine *C*H), 128.9 (ArCH), 126.3 (CpC), 126.2 (ArCH), 34.6 (*i*-Pr *C*H), 24.5 (*i*-Pr C*Me*$_2$) ppm. Anal. Calcd for $C_{124}H_{126}N_4O_4Sm_2$: C, 73.11%; H, 6.23%; N, 2.75%. Found: C, 73.05; H, 6.24%; N, 2.73%.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00254.

Experimental procedures for attempts to react **1** with CO, $CO_2$, $N_2$, pyrazine, stilbene, pyridine, $P_4$, ethylene, styrene, phenazine, benzophenone, fluorenone and benzoquinone; Selected $^1$H NMR spectra of products; Details for crystal structure determinations (PDF)

### Accession Codes

CCDC 1838409−1838412 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219−223. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6507−6508. (c) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270−4272.

(2) Evans, W. J.; Giarikos, D. G.; Robledo, C. B.; Leong, V. S.; Ziller, J. W. *Organometallics* **2001**, *20*, 5648−5652.

(3) Evans, W. J.; Drummond, D. K.; Hughes, L. A. *Polyhedron* **1988**, *7*, 1693−1703.

(4) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314−2324.

(5) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877−6879.

(6) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *Inorg. Chem.* **1998**, *37*, 770−776.

(7) Sitzmann, H.; Dezember, T.; Schmitt, O.; Weber, F.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2241−2244.

(8) Weber, F.; Sitzmann, H.; Schultz, M.; Sofield, C. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 3139−3146.

(9) Selikhov, A. N.; Mahrova, T. V.; Cherkasov, A. V.; Fukin, G. K.; Larionova, J.; Long, J.; Trifonov, A. A. *Organometallics* **2015**, *34*, 1991−1999.

(10) (a) Ruspic, C.; Moss, J. R.; Schürmann, M.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2121−2126. (b) Harder, S.; Naglav, D.; Ruspic, C.; Wickleder, C.; Adlung, M.; Hermes, W.; Eul, M.; Pöttgen, R.; Rego, D. B.; Poineau, F.; Czerwinski, K. R.; Herber, R. H.; Nowik, I. *Chem. - Eur. J.* **2013**, *19*, 12272−12280.

(11) (a) Deacon, G. B.; Forsyth, C. M.; Jaroschik, F.; Junk, P. C.; Kay, D. L.; Maschmeyer, T.; Masters, A. F.; Wang, J.; Field, L. D. *Organometallics* **2008**, *27*, 4772−4778. (b) Kelly, R. P.; Bell, T. D. M.; Cox, R. P.; Daniels, D. P.; Deacon, G. B.; Jaroschik, F.; Junk, P. C.; Le




DOI: 10.1021/acs.organomet.8b00254
*Organometallics* 2018, 37, 2263−2271

Goff, X. F.; Lemercier, G.; Martinez, A.; Wang, J.; Werner, D. *Organometallics* **2015**, *34*, 5624−5636.
(12) Field, L. D.; Lindall, C. M.; Masters, A. F.; Clentsmith, G. K. B. *Coord. Chem. Rev.* **2011**, *255*, 1733−1790.
(13) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827−841.
(14) Harder, S. *Chem. - Eur. J.* **2013**, *19*, 12272−12280.
(15) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435−3449.
(16) Orzechowski, L.; Piesik, D. F.-J.; Ruspic, C.; Harder, S. *Dalton Trans.* **2008**, 4742−4746.
(17) Desiraju, G. R. *Chem. Commun.* **2005**, 2995−3001.
(18) Kuchenbecker, D.; Jansen, G.; Harder, S. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2257−2261.
(19) Wagner, J. P.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **2015**, *54*, 12274−12296.
(20) Liptrot, D. J.; Power, P. P. *Nat. Rev. Chem.* **2017**, *1*, 0004.
(21) Dyker, G.; Heiermann, J.; Miura, M.; Inoh, J.-I.; Pivsa-Art, S.; Satoh, T.; Nomura, M. *Chem. - Eur. J.* **2000**, *6*, 3426−3433.
(22) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728−3730.
(23) Selg, P.; Brintzinger, H. H.; Schultz, M.; Andersen, R. A. *Organometallics* **2002**, *21*, 3100−3107.
(24) Evans, W. J.; Perotti, J. M.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5204−5212.
(25) Castro, L.; Labouille, S.; Kindra, D. R.; Ziller, J. W.; Nief, F.; Evans, W. J.; Maron, L. *Chem. - Eur. J.* **2012**, *18*, 7886−7895.
(26) Davies, N. W.; Frey, A. S. P.; Gardiner, M. G.; Wang, J. *Chem. Commun.* **2006**, 4853−4855.
(27) Khuong, K. S.; Jones, W. H.; Pryor, W. A.; Houk, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 1265−1277.
(28) (a) Baudler, M.; Glinka, K. *Chem. Rev.* **1993**, *93*, 1623−1667. (b) Yakhvarov, D. G.; Gorbachuk, E. V.; Sinyashin, O. G. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4709−4726. (c) He, G.; Shynkaruk, O.; Lui, M. W.; Rivard, E. *Chem. Rev.* **2014**, *114*, 7815−7880. (d) Cossairt, B. M.; Piro, N. A.; Cummins, C. C. *Chem. Rev.* **2010**, *110*, 4164−4177.
(29) Kraus, F.; Aschenbrenner, J. C.; Korber, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 4030−4033.
(30) Kraus, F.; Korber, N. *Chem. - Eur. J.* **2005**, *11*, 5945−5959.
(31) Abicht, H.-P.; Hönle, W.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1984**, *519*, 7−23.
(32) Schmettow, W.; Lipka, A.; Von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 345.
(33) Von Schnering, H. G.; Meyer, T.; Hönle, W.; Schmettow, W.; Hinze, U.; Bauhofer, W.; Kliche, G. *Z. Anorg. Allg. Chem.* **1987**, *553*, 261−279.
(34) Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J. *Z. Naturforsch., B: J. Chem. Sci.* **1979**, *34b*, 1690−1697.
(35) Konchenko, S. N.; Pushkarevsky, N. A.; Gamer, M. T.; Köppe, R.; Schnöckel, H.; Roesky, P. W. *J. Am. Chem. Soc.* **2009**, *131*, 5740−5741.
(36) Ahlrichs, R.; Brode, S.; Ehrhardt, C. *J. Am. Chem. Soc.* **1985**, *107*, 7260−7264.
(37) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600−2608.
(38) De Boer, E. *Adv. Organomet. Chem.* **1965**, *2*, 115−155.
(39) Evans, W. J.; Schmiege, B. M.; Lorenz, S. E.; Miller, K. A.; Champagne, T. M.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 8555−8563.
(40) Nechaeva, O. N.; Pushkareva, Z. V. *Zh. Obshch. Khim.* **1958**, *28*, 2693.
(41) Carlson, C. N.; Kuehl, C. J.; Da Re, R. E.; Veauthier, J. M.; Schelter, E. J.; Milligan, A. E.; Scott, B. L.; Bauer, E. D.; Thompson, J. D.; Morris, D. E.; John, K. D. *J. Am. Chem. Soc.* **2006**, *128*, 7230−7241.
(42) Labouille, S.; Nief, F.; Le Goff, X.-F.; Maron, D.; Kindra, D. R.; Houghton, H. L.; Ziller, J. W.; Evans, W. J. *Organometallics* **2012**, *31*, 5196−5203.
(43) Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154−7160.
(44) Baker, E. C.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 2710−2714.
(45) Lopes, I.; Dias, R.; Domingos, A.; Marques, N. *J. Alloys Compd.* **2002**, *344*, 60−64.
(46) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754−766.
(47) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405−409.
(48) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828−7829.
(49) Deng, D.-L.; Zhang, Y.-H.; Dai, C.-Y.; Zeng, H.; Ye, C.-Q.; Hage, R. *Inorg. Chim. Acta* **2000**, *310*, 51−55.
(50) Janiak, C.; Weimann, R.; Görlitz, F. *Organometallics* **1997**, *16*, 4933−4936.
(51) Evans, W. J.; Miller, K. A.; Lee, D. S.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 4326−4332.
(52) Yeh, W.-Y.; Ho, C.-L.; Chiang, M. Y.; Chen, I.-T. *Organometallics* **1997**, *16*, 2698−2708.
(53) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421−4422.
(54) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2815−2817.
(55) Butman, L. A.; Sokol, V. I.; Porai-Koshits, M. A. *Koord. Khim.* **1976**, *2*, 265−271.
(56) Banres, J. C.; Blyth, C. S.; Paton, J. D. *Lanth. Actin. Res.* **1990**, *3*, 181−193.
(57) Neumüller, B.; Weller, F.; Gröb, T.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2365−2371.
(58) Jankowski, W.; Gdaniec, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *C58*, o181−o182.
(59) Harder, S.; Ruspic, C.; Ní Bhriain, N.; Berkermann, F.; Schürmann, M. *Z. Naturforsch.* **2008**, *63b*, 267−274.
(60) Jing, X.; Pan, X.; Li, Z.; Shi, Y.; Yan, C. *Synth. Commun.* **2009**, *39*, 492−496.



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*Organometallics* 2018, 37, 2263−2271